

MODEL FOR COMBUSTION OF TRIPLE-BASE PROPELLANT WITH DETAILED CHEMISTRY

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ABSTRACT

A model including detailed gas phase chemistry previously applied to nitrate ester and nitramine solid propellants and their major ingredients has been successfully applied to the pure energetic ingredient nitroguanidine and to M30, a triple base propellant which contains nitroguanidine. This is the first modeling of either based on a detailed gas phase mechanism. Computed burning rates are in reasonable agreement with experiment. Predicted flame structures indicate the unusual result that no dark zone forms even at low pressure (0.5 MPa), in agreement with experiment; detailed chemical analysis conclusively indicates the lack of a dark zone is due to rapid gas phase reactions of NH and NH₂ species with NO. Our expansion of the universe of ingredients successfully modeled with our approach bodes well for its use in formulation science and its transfer, as reduced versions, into interior ballistics weapons development codes.

1. INTRODUCTION

Gun and rocket propellant science would be greatly aided by the availability of models to predict important characteristics. One of the most crucial performance parameters of a solid propellant is the one-dimensional steady-state burning rate, and its dependence on pressure and unburned-propellant temperature. Models for predicting combustion characteristics, such as the rate and flame structure, based on elementary flame reactions (tens of species, hundreds of reactions) and transport properties have been under development since about the mid 1980s. Inclusion of detailed chemistry is necessary to accurately predict the effects of propellant formulation changes and gas phase characteristics. Applications have been limited to idealized ‘propellants’ containing only one or a few ingredients, primarily due to currently insurmountable problems obtaining detailed input information about the condensed phase processes. Recently we developed a new approach (Miller and Anderson, 2000) to the prediction of burning rates that finesses this problem by using a semi-empirical method:

a universal pyrolysis law for a given class of propellants relates the surface temperature to the burning rate, and the nascent gas-phase product distribution is obtained by a non-interacting superposition of products for each ingredient in the propellant formulation. In this way, a promising predictive capability was achieved and applied to pure ingredients and simple mixtures.

Our new approach has recently allowed the first successful modeling of actual, complex-mixture propellants, including several current U.S. Army-fielded nitrate ester (Miller and Anderson, 2004), and developmental nitramine/ETPE-binder propellants (Miller and Anderson, 2003a). An accurate predictive tool has long been sought by propellant formulators; this work is nearing fulfillment of that goal. In addition, the method only requires spatial resolution of the gas phase – the condensed phase modeling is greatly simplified vs. earlier 3-phase methods. This has made it feasible to include our model in a more complex engineering application: reduced versions for specific propellants have recently been included in a complex CFD model of electrothermal – chemical plasma - propellant gun ignition experiments (Nusca et al, 2004), strongly enhancing the rigor of that work. This suggests reduced models based on our approach might even be included in interior ballistics codes in the near future, thus having a major influence on gun and rocket weapon system development. It is therefore important to expand our capabilities to new ingredients, and applications to new propellant mixtures.

In the present work, the first successful combustion modeling of the important energetic material nitroguanidine (NQ) and an associated triple base propellant, M30, is reported. The latter is complex, being composed of nitrocellulose (NC), nitroglycerine (NG), and NQ. The work contains several important advances besides simply prediction of burning rates. First, NQ is a crystalline fill energetic material which may pose challenges to one-dimensional modeling. Also, M30 burns without a dark zone in its flame structure, even at low pressures, and this unusual feature is properly predicted by our model. Finally, through detailed chemical-kinetic

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analysis of the solutions, the lack of a dark zone* is found to be due to the unusual flame chemistry of NQ's gaseous products. This chemistry is related to that of burning rate modifier additives, an important area for possible applications of extreme interest for formulation science. Also, recent work has established that low pressure dark zone chemistry is much more important to combustion behavior at high pressures pertinent to guns than *anyone* previously thought (Miller and Anderson, 2004). Therefore, we studied the detailed chemistry using our advanced chemical pathways and sensitivity analysis codes. The results are herein discussed.

In summary, the burning rates and flame structure for NQ and M30 have been successfully predicted using our new modeling approach. The results and details of the flame chemistry will be presented. This is yet another example of the promise of our new semi-empirical pyrolysis-law model. Large savings of time and funds should eventually result for development of guns, rockets, and associated propellants pertinent to FCS and other weapons systems.

2. MODELING APPROACH

Solid propellant combustion models have long been plagued by lack of methods to obtain rigorous input information about the condensed phase processes. To overcome this impasse, we recently proposed a hybrid-rigor approach and applied it to nitrate ester and nitramine propellants (Miller and Anderson, 2000, 2003a, 2004). Briefly, the method allows one to totally ignore spatial modeling of the condensed phase processes; rather, one simply computes the heat feedback requirement to gasify the condensed phase mixture to initial gas phase intermediates (dubbed 'surface products'). The propellant mixture is first classified, e.g. as nitrate ester or nitramine. A pyrolysis law is separately obtained from experiments on a large variety of propellants within broad classes; the appropriate one for the mixture of interest is selected. This 'law' (actually parameters for a fitted equation) relates the surface temperature to the gaseous mass flux out of the surface. When used in our model, one assumes a mass flux (easily related to the burning rate) and uses the 'law' to determine surface temperature. We also mentioned a surface product distribution is assumed for each ingredient; its temperature at formation is assumed equal to the surface temperature. Thus, the enthalpy difference between starting propellant mixture and gas-phase surface products is easily calculated. Combining this difference with the mass flux, one obtains the condensed phase heat feedback requirement for steady-state combustion. Note the surface products, surface

temperature, and mass flux uniquely define a one-dimensional, premixed laminar flame problem. This problem is next solved. From the gas phase structure of the solution, in particular the near surface temperature gradient and physical characteristics, one can derive the heat flux being driven from the flame into the surface. An algorithm iterates on mass flux in such manner as to cause convergence of the condensed phase heat flux requirement to the heat supplied by the gas phase flame.

Once the problem has converged, the burning rate is obvious. The chemistry of the gas phase structure corresponding to the solution can also be interrogated. Codes we have written allow dissection of the complex chemistry using rate flux (pathway) analysis to obtain the fastest reactions, and also those reactions to which the solution is most sensitive (which for a number of well-known reasons may differ from the fastest reactions). As will be seen, these techniques allow an interesting comparison of M30 gas phase chemistry to our prior results for nitrate ester propellants.

It should be noted that for propellant predictions agreement for absolute burning rate values within a factor of 2 is considered reasonable in this type work since there are so many input parameters and, once the fit for individual ingredients has been accomplished, no parameters are further manipulated for the propellant mixtures. One hopes the relative trends vs. pressure will match within better than a factor of two.

M30 propellant is composed primarily of nitrocellulose (NC) at a nitration level of 12.6% N, nitroglycerine (NG), and nitroguanidine (NQ) (mass fractions 0.285, 0.229, and 0.486, respectively). Though NQ has NH_x moieties, its main energetic component is due to its nitramine moiety. It is known from experiments (Zenin et al, 2000) that the proper pyrolysis law for nitramines mixed into nitrate esters (CMDB, composite-modified double base propellants) is that for pure nitrate ester propellants, so this law was chosen. The related parameters and also modeling inputs for NC and NG may be found in Miller and Anderson, 2003b. Inputs for NQ, first modeled in this work, are discussed in the next section. The detailed gas phase mechanism of 59 species, 365 reactions is also from Miller and Anderson, 2003b.

3. NITROGUANIDINE (NQ) RESULTS AND DISCUSSION

Pyrolysis experiments on NQ, $\text{C}(\text{NH}_2)_2\text{NNO}_2$, indicate that large quantities of NH_3 , amongst other gaseous species, may be formed (Oyumi et al, 1987). It must be kept in mind that the species observed in such experiments generally are not believed to be the initial surface products because significant gas phase reactions cannot be quenched in experiments. Thus, it is quite possible that

* Nonluminous gaseous region between solid propellant surface and final hot, luminous flame.

precursors of the species mentioned may initially form during combustion. It is our general approach to test a wide variety of surface product sets and select a set most compatible with combustion data for the pure ingredients. Sets are chosen to be compatible with chemical intuition and as precursors of species observed in pyrolysis experiments. Once a workable set is found for a given ingredient it is then fixed and used for the ingredient in mixtures. For NQ, the best gaseous set found is: $\text{NQ(s)} \rightarrow \text{NO}_2 + \text{HCN} + \text{NH}_2 + \text{NH}$. There are experimental burning rate data for NQ, but no flame structure data.

The burning rate results for NQ are compared to experimental results from the computer database FLAME (Fogelzang et al, 1991-96) in the typical log-log plot, see Fig. 1. As may be seen, the comparison is good at pressures of 4 MPa (~ 40 atm) and above. The absolute values match to within about 30%. Note the noise in the experimental data is of similar magnitude to the differences. Below 4 MPa, there is a strong deviation between theory and experiment. The experimental results suddenly trend strongly downwards from a linear extrapolation (on the log-log plot) of the higher pressure results, while the predicted values do not. It should be noted that such a strong bend in burning rate plots is unusual for most solid propellants or their neat energetic ingredients. Other nitramines, such as RDX, HMX, and CL20, do not exhibit this behavior. And there is no known intuitive reason to expect a strong mechanism change (for example, as the surface temperature increases with higher pressure). On the other hand, the burning rates are much slower than for other nitramines (not shown). This is suggestive that at the lower pressures in Fig. 1, the experiments may approach a low pressure deflagration limit. This limit is a function of propellant strand size, because as it is approached, heat losses to surroundings at the edge become very important. This is a non-one-dimensional effect, and thus the model may be more indicative of one-dimensional behavior than the data. Therefore, no further attempt to better match the low pressure data was made.

4. M30 PROPELLANT RESULTS AND DISCUSSION

Burning rate results for M30 are shown in Fig. 2. As can be seen, the predictions are parallel to experimental results, but higher by about a factor of 1.5 to 2, across a wide range of pressure, up to and including pressures pertinent to guns. The experimental results are even suggestive of a slight downwards curvature which is well-reproduced in the predictions. The agreement is fairly good.

There are no instrumentally based measurements of the flame structure of M30 flames at any pressure (e.g. by spatially resolved spectroscopic or mass spectral sampling, as has been done for other propellants). However, Miller noted in his work resulting in the burning rates of Fig. 2 that M30 exhibits no dark zone at any pressure, even the lowest at 0.25 MPa (unpublished visual observations). Also, Miller and Vanderhoff have made video movies of combustion of various propellants in a windowed strand burner (Miller and Vanderhoff, 2001). The recording at 0.5 MPa shows M30 burns with a bright yellow visible flame.[†] The flame seats very close to the propellant surface, that is, there is no dark zone. Most propellants do exhibit a dark zone at pressures below ~ 10 MPa, with dark zone length varying roughly inversely with pressure.

The lack of profile measurements for M30 precludes verification of our flame structure predictions. However, our predictions at least agree with the visual observation that no dark zones form. Profiles of temperature and several major species at 1.0 MPa are shown in Fig. 3. The temperature begins rising rapidly near the surface to the adiabatic flame temperature, with no evidence of a plateau. The species profiles also reflect a rapid conversion from surface products to final flame products. Note that NO does form near the surface, but it rises to a maximum and begins to decay fairly close to the surface, a typical behavior of an intermediate that is primarily formed and consumed in a narrow flame.

In contrast to M30, we show predicted profiles for M10 at 1.0 MPa (Miller and Anderson, 2004), see Fig. 4. M10 is composed primarily of NC (13.1% N). Its dark zone behavior is typical of propellants composed solely of nitrate esters, including all those we studied. Note for M10 the temperature profile rises rapidly above the surface to an intermediate value and then forms a plateau. The temperature only rises slowly up to about 1 cm and then much more rapidly somewhere between 1 and 2 cm. The plateau region corresponds to the dark zone region observed in experiments. (The plateau region is from about 0.2 to 1.0 cm and perhaps as high as about 1.7 cm. There is a hump at about 1.3 cm that obscures exactly where the dark zone ends. Chemistry related to this hump is discussed in detail for three propellants in Miller and Anderson, 2004.) The major species profiles are also indicative of this behavior. The NO intermediate species is of particular import because its slow reaction in the dark zone is the primary reason for dark zone formation. The prediction indicates its concentration rises rapidly near the propellant surface. In the dark zone region, NO exhibits a

[†] The color is likely due to NH_2 , a known strong yellow emitter, arising from the major NQ ingredient. Na, another strong yellow emitter, is not in any of the ingredients so would only arise as an impurity and as such not yield strong emission. NH_2 would not survive long in a dark zone because of rapid reaction with major dark zone species NO.

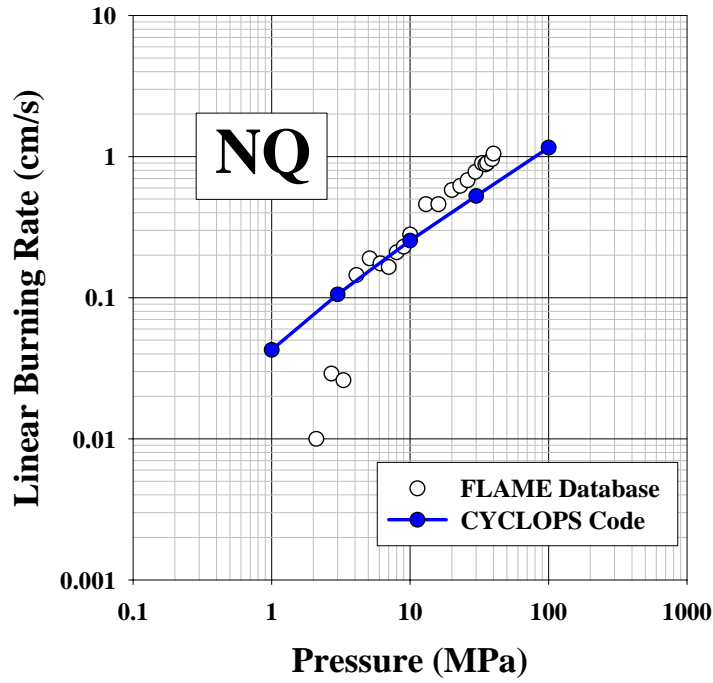


Fig. 1. Burning rate plot for NQ.

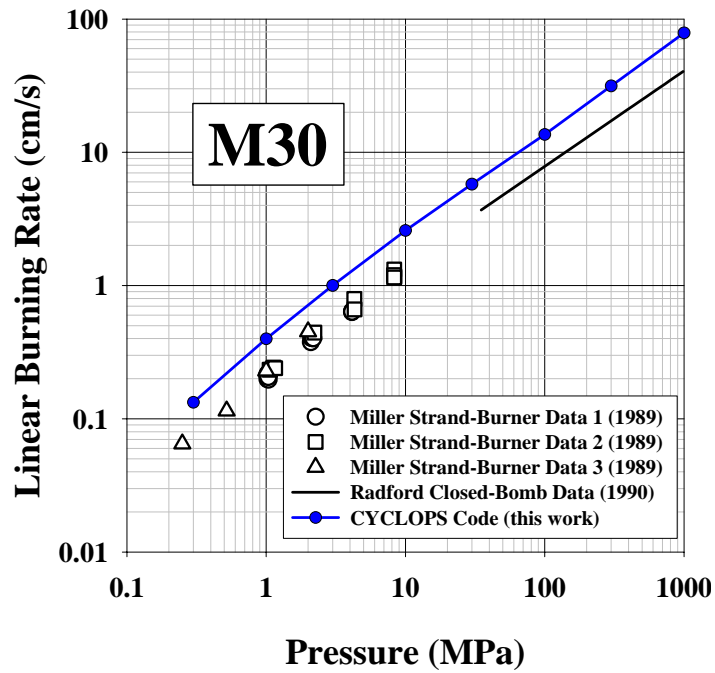


Fig. 2. Burning rate plot for M30.

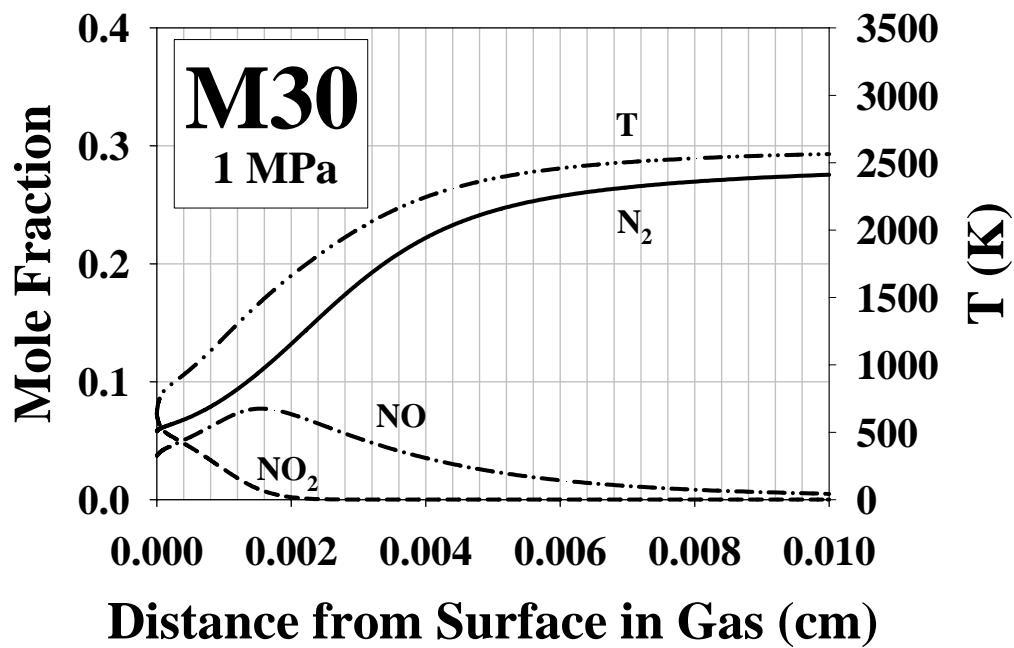


Fig. 3. Profiles of temperature and selected nitrogenous species in an M30 flame at 1.0 MPa.

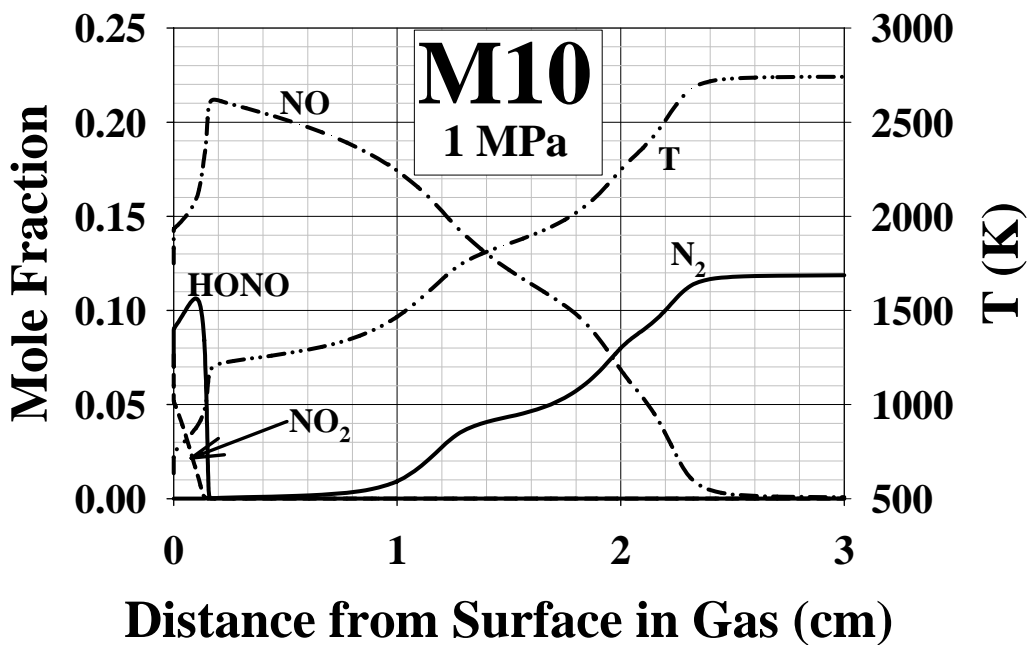


Fig. 4. Profiles of temperature and selected nitrogenous species in an M10 flame at 1.0 MPa.

slow decay until it suddenly begins reacting rapidly, in concert with the temperature rise at about 1 to 2 cm. The final product N_2 also rises as the NO is consumed. Further discussion of dark zone formation for nitrate esters and comparison of predicted and measured flame structures is given in Miller and Anderson, 2004. The fact that a comprehensive model properly predicts the dark zone formation, or lack thereof, for a variety of propellants is quite gratifying.

We have speculated for almost 10 years that the reason M30 exhibits no dark zone in its flame structure is that NH_x species ($x = 1,2,3$), which arise near the propellant surface from the presence of NQ, react rapidly with NO resulting in rapid conversion to final product N_2 . This rapid conversion is not possible for most propellants because NO intermediate is surprisingly unreactive with most commonly available intermediate species. NH and NH_2 , however, react extremely rapidly with NO, even at room temperature; thus, fast conversion is possible with NQ. Detailed rate analysis confirms for the first time that presence of these species indeed is the reason for the lack of dark zone formation for M30.

Chemical pathways diagrams for the nitrogenous species, constructed from the rate analysis results, illustrate the difference between M30 and a typical nitrate ester propellant, M10, in Figs. 5 and 6. The diagrams are based on relative rates of reactions integrated over a short spatial slab above the propellant surface (that is, typical units are mole/cm²-s, with the largest normalized to 100 in the figures). The integration limits are from zero (the surface) to one characteristic heat transfer distance (distance at which effectiveness of heat release in reaching the surface drops by 1/e; see Miller and Anderson, 2004). In Fig. 5, the result for M10 at 10 atm is shown. The diagram is fairly simple, with only five nitrogenous species playing a major role. The main N-species reaction occurring near the surface is NO_2 conversion to NO. Little conversion to N_2 takes place near the surface.

The comparable diagram for M30 at 10 atm, Fig. 6, is considerably more complicated than that of M10. As for M10, there is still an important conversion of NO_2 to NO occurring. However, even within a short distance above the surface, there is significant conversion of NO to N_2 and N_2O . The conversion occurs almost entirely due to reactions of NH or NH_2 with NO. It should be noted that N_2O is converted to N_2 much more readily than NO; although this does not happen in the very short slab studied, it certainly happens in a shorter distance than otherwise possible.

The assignment of the dark zone differences for M30 vs nitrate esters to NH_x chemistry with NO is also confirmed by inspection of the sensitivity of computed

temperature near the propellant surface to rate coefficients for the various gas phase reactions (sensitivity analysis, to be published). For M30, the sensitive reactions include several between NH_x species and NO. For M10, the reactions do not appear because the NH_x species are not significant intermediates.

5. CONCLUSION

The combustion of NQ and M30 has been successfully modeled with detailed chemistry using our semi-empirical approach. Burning rate results for NQ were fitted to experimental values using an initial condensed phase gaseous product set that is compatible with pyrolysis experiments and chemical intuition. The NQ inputs were then fixed and used to predict burning rates for a fielded propellant, M30. The absolute burning rates are in reasonable, and the relative rates in excellent, agreement with experiment. It is especially gratifying that the predicted, unusual, lack of a dark zone for M30 even at low pressures agrees with experiment. This result is shown to be due to the presence of NH_x species, arising from the NQ ingredient, which react rapidly with NO resulting in ultimate formation of final product N_2 near the propellant surface. This rapid conversion of NO to N_2 is not possible for most other propellants, resulting in dark zone formation.

With this work, the utility of our semi-empirical approach is shown for another ingredient and for a triple-base propellant. Besides prediction of the burning rates, which is very important to formulation science, we have shown the dark zone structure can be properly predicted for a variety of propellant types. This ability is extremely important for two reasons. First, contrary to prior thought in the community, the reactions controlling the dark zone structure (in particular its length) at low pressures have been shown to strongly affect the burning rates at high pressures (Miller and Anderson, 2004). Second, the characteristics of dark zone mixtures, if they form, are thought to have a major influence, contributing to undesirably long gun ignition delays (Kooker et al, 1995, 1996). Use of ingredients like NQ to mitigate NO formation during early flamespreading stages of interior ballistic cycles could ultimately lead to shortened delay times, a very desirable result.

In prior work, we have suggested the use of propellant additives which produce intermediates NH_x and HNCN could yield control over burning rate. The present work is a first step in modeling NQ as such an additive, and in understanding the role of NH_x species in making the temperature gradient near the surface steeper.

All of these results, and the inclusion of our more sophisticated models in weapon development codes, will

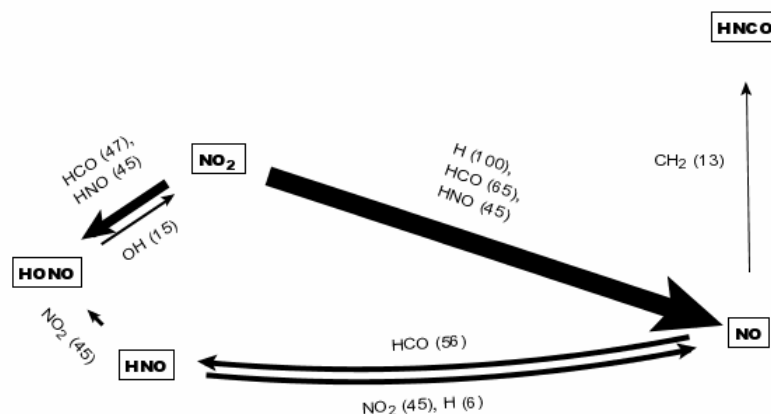


Fig. 5. Nitrogenous species pathway diagram for M10 at 1.0 MPa. The reaction rates are integrated from the surface to the characteristic heat transfer distance, 5.51×10^{-4} cm. The relative rate of 100 is 2.15×10^{-3} mole/cm²-s.

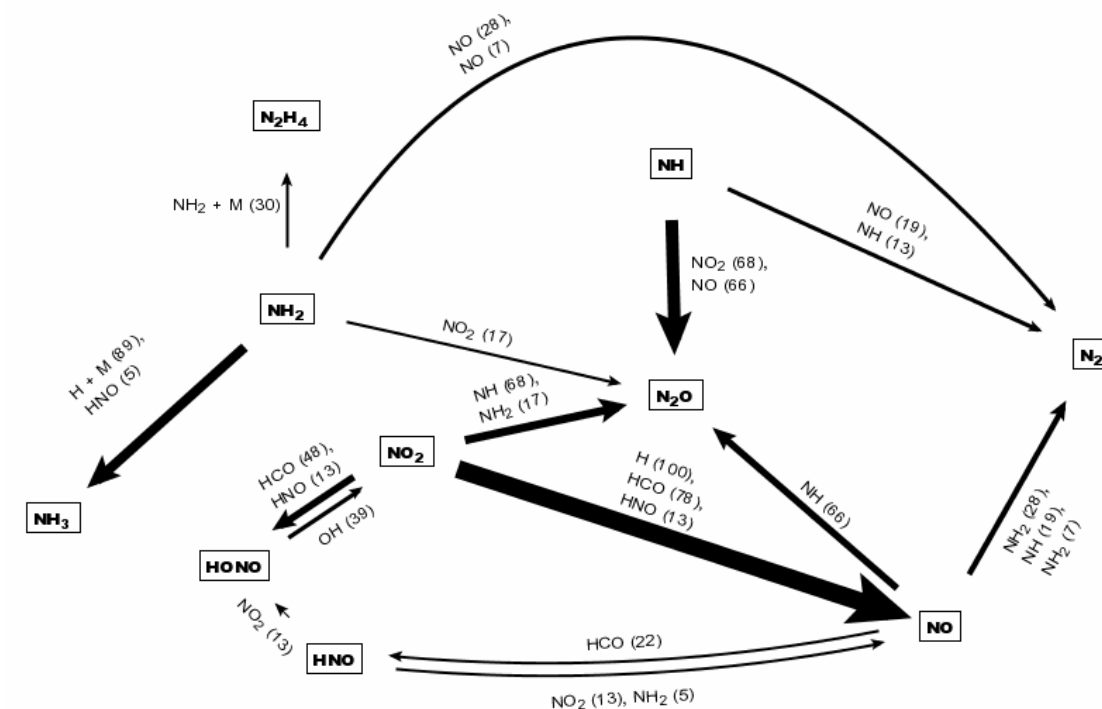


Fig. 6. Nitrogenous species pathway diagram for M30 at 1.0 MPa. The reaction rates are integrated from the surface to the characteristic heat transfer distance, 6.39×10^{-4} cm. The relative rate of 100 is 1.75×10^{-3} mole/cm²-s.

ultimately make the development of weapons systems timelier and less costly than the present trial-and-error approach.

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